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# THERMOGRAVIMETRIC STUDY OF OXIDATION OF A PdCr ALLOY USED FOR HIGH-TEMPERATURE SENSORS

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## SUMMARY

In this study, the oxidation of Pd-13wt%Cr, a candidate alloy for high-temperature strain gages, was investigated by thermogravimetry. Although the bulk alloy exhibits linear electrical resistivity versus temperature and stable resistivity at elevated temperatures, problems attributed to oxidation occur when this material is fabricated into strain gages. In this work, isothermal thermogravimetry (TG) was used to study the oxidation kinetics. Results indicate that the oxidation of Pd-13wt%Cr was approximately parabolic in time at 600 °C but exhibited greater passivation from 700 to 900 °C. At 1000 °C, the oxidation rate again increased.

## INTRODUCTION

Pd-13wt%Cr (henceforth referred to as PdCr) is a solid solution that has shown promise as a material for high-temperature strain gages and possesses a number of intrinsic characteristics desirable for such an application. The bulk alloy has a relatively high melting point of 1397 °C and displays stable electrical resistance in air at 1000 °C. Its electrical resistance not only varies linearly with temperatures above 1000 °C, but is also independent of the heating or cooling rates. It also exhibits strong adhesion to alumina, which is used to provide electrical isolation between the substrate and the sensor material. Additionally, formation of an adherent, self-protective chromium oxide film provides the bulk alloy with good oxidation resistance (ref. 1).

Although the oxidation self-protection is sufficient for the bulk material, it is insufficient when the alloy is fabricated into structures with high surface-to-volume ratios (ref. 2). Current resistive strain gage technology utilizes very fine wires (as small as 25- $\mu$ m-diam) or thin films (10- $\mu$ m-diam). When PdCr is fabricated into these structures and tested in air at temperatures above 600 °C, unstable electrical resistance is observed. This sensor failure problem may be attributed to oxidation of the alloy. Only when they have been covered with a protective overcoats have these gages been able to perform at higher temperatures (ref. 3).

In this study isothermal thermogravimetry (TG) was used to study oxidation kinetics of PdCr. Thermogravimetrics is a thermal analysis technique in which a thermobalance is employed to measure the weight of a sample as it is subjected to a controlled temperature. With isothermal TG, sample weight is recorded as a function of time at constant temperature. For a sample in an oxygen-containing atmosphere, weight gain can be attributed to oxidation. Analysis of a sample weight plot versus time can be used to determine the oxidation kinetics.

## EXPERIMENT

To study the oxidation kinetics of PdCr, three sets of TG experiments were conducted. The first set utilized wire samples in a mixture of air and argon at 600, 800, and 1000 °C; the second set utilized ribbon samples in oxygen at 400, 600, and 800 °C; and the third set utilized ribbon samples in air at 600, 700, 800, and 900 °C.

### Samples

The samples used for analysis consisted of wires and ribbons fabricated from bulk Pd-13wt%Cr (nominal composition). Wire samples were 70  $\mu$ m in diameter and approximately 50 mg in weight. The wire was supplied by Battelle-Columbus Laboratories and was produced by casting and drawing, followed by annealing. Ribbon samples were 70  $\mu$ m thick, 2.5 mm wide, and approximately 20 mg in weight. The ribbon was produced at the NASA Lewis Research Center by a spin-melt process in which the alloy was quenched from the melt. These different processing procedures resulted in the wire's being subjected to substantially more cold working and annealing than the ribbon.

### Analysis

Thermogravimetric data were collected on wire and ribbon samples as listed in table I. In all cases, the gas flow rate was approximately 60 cc/min. The TG was approximately isothermal with the exception of the relatively short heating time from the initial to the run temperature at the heating rate (table 1). The run temperature was then maintained for approximately 20 hr while the weight of the sample was recorded.

## RESULTS

Results of the set of experiments utilizing wire samples are shown in figure 1 and results of the two sets of experiments utilizing ribbon samples are shown in figures 2 and 3. All three sets of experiments showed the same general trends with respect to temperature and therefore all three sets will be discussed together.

In figures 1 to 3, weight percent (or specific weight) is plotted versus time. In the following discussion, it is most often natural to talk in terms of the rate of weight gain, which is the derivative with respect to the time of the weight percent (or specific weight) versus time plot. No weight gain was observed at 400 °C, the lowest temperature investigated, indicating that no significant oxidation occurred.

At 600 °C, all three samples exhibited weight gain, indicating that significant oxidation did occur. The initial rates of weight gain were slow compared with those at higher temperatures. However, in comparison with the higher temperatures, the rates decreased only gradually with time.

The sample at 700 °C exhibited behavior intermediate to that seen at 600 °C and at 800 to 900 °C (fig. 3). The rate during the initial gain was fast in comparison with that at 600 °C but was comparatively slow at 800 and 900 °C. After approximately 3 hr, the rate decreased to the point where it was slow compared with that at 600 °C but, the decrease was much less than the decrease seen at 800 and 900 °C. After about 4.5 hr, the weight percent of the 700 °C sample was less than the weight percent of the 600 °C sample.

At 800 and 900 °C, all samples initially showed very rapid weight gain followed by an abrupt plateau in this gain. The changes in the slopes of these curves indicate surface passivation (fig. 3). The sample at 1000 °C (fig. 1) also exhibited a rapid initial weight gain that was followed by only a gradual decrease in the rate.

## DISCUSSION

Under certain simplifying assumptions, Wagner (ref. 4) developed expressions for the rate of bulk-diffusion-controlled oxidation. Wagner's theory predicts that weight gain versus time is parabolic if the rate-limiting step during oxidation is diffusion through a thickening protective scale. When the weight gained during oxidation is plotted against the square root of time, parabolic weight gain appears as a straight line. From the slope of the straight line a parabolic rate constant can be determined.

The data from figure 2 were replotted with specific weight plotted against the square root of time (fig. 4). The oxidation at 600 °C is approximately parabolic with respect to time. In contrast, the oxidation at 800 °C is not parabolic with respect to time, but instead it exhibits a downward curvature indicating greater passivation than parabolic oxidation. After 10 to 12 hr, the data for the 600 °C ribbon show a slight upward turn from the straight line, which could be caused by cracking in the protective oxide layer. Cracking would permit oxygen to penetrate directly to the underlying metal and would be expected to cause an upward turn in the data or an increase in the oxidation rate.

From the slope of the straight line portion of the 600 °C curve (fig. 4), a parabolic rate constant of  $1.5 \times 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$  was determined. Since Auger electron spectroscopy studies indicate that the oxide scale on PdCr is composed of  $\text{Cr}_2\text{O}_3$  (ref. 2), a comparison can be made with rate constants for this formation. The rate constant is expected to increase rapidly with increasing temperature because of faster ionic diffusion, therefore, a correction for temperature must be made.

Hughes et al. (ref. 5) have plotted the logarithm of the measured values of the rate constant against inverse temperature. The measured values show a large variation at temperatures above 800 °C with the rate constant at 900 to 950 °C being about 1.5 to 5 orders of magnitude larger than at 600 °C. When this temperature correction is applied, the measured rate constant is approximately 1 order of magnitude less than that found by Polman et al. (ref. 6) for  $\text{Cr}_2\text{O}_3$  growing on pure chromium at 900 °C under a variety of oxygen partial pressures. The measured rate constant is also slightly more than 1 order of magnitude less than that found by Skeldon et al. (ref. 7) for  $\text{Cr}_2\text{O}_3$  growing on pure chromium at 950 °C in 1 atm of oxygen.

The value of the rate constant determined at 600 °C (fig. 4) is at least slightly larger than expected. However, the values from Polman et al. (ref. 6) and Skeldon et al. (ref. 7) were for  $\text{Cr}_2\text{O}_3$  growing on pure chromium whereas PdCr contains only 13 wt % chromium. The difference in alloy composition's affect on the rate constant is not obvious, but since the rate constant is directly related to the diffusivity through the protective oxide scale, anything that changes the nature of that scale can affect the rate constant.

The 800 °C data from figure 4 show a downward curvature indicating that the oxidation rate is slower than parabolic rate. Kofstad and Lillerud (ref. 8) saw similar behavior for the oxidation of pure chromium at 800 °C in 1 atm of oxygen and attributed the behavior to a decrease in the number of short-circuit diffusion paths with time. Several studies have found that when PdCr oxidizes, a layer of metallic palladium forms on the surface (refs. 2, 9, and 10). The morphology of this layer depends on the temperature and time of oxidation.

Since most researchers believe the solubility and diffusivity of oxygen in palladium are relatively high (refs. 11 to 13), it would be expected that a surface layer of metallic palladium would have little effect on the oxidation rate. However, metallic palladium included in a chromium oxide scale could provide a pathway for oxygen diffusion through the scale. The resulting short-circuit paths of metallic palladium could have a large effect on the oxidation rate. If the number of palladium inclusions were to decrease with time, the oxidation rate could show the observed behavior. Such short-circuit paths could also explain the anomalously high value of the rate constant observed at 600 °C.

The large weight gain seen at 1000 °C (fig. 1) is a result of the increased diffusion expected at higher temperatures. From 700 to 1000 °C chromium diffusion in  $\text{Cr}_2\text{O}_3$  increases by more than 3 orders of magnitude and oxygen diffusion by more than 5 orders of magnitude (ref. 14). However, since the oxidation is not parabolic above 600 °C, a parabolic rate constant cannot be determined and therefore a quantitative comparison cannot be easily made.

Further evidence that the oxidation of chromium is responsible for the weight gains is derived from the calculation of the total possible weight gained from the oxidation of all of the chromium. If all the chromium in PdCr was oxidized to  $\text{Cr}_2\text{O}_3$ , a weight gain of about 6 percent would be expected. Since the largest total weight gained in any of the experiments was less than 3 percent, oxidation of chromium could completely account for all the weight gains.

At temperatures below about 870 °C (at 1 atm partial pressure of oxygen), PdO is thermodynamically stable. However, Auger electron spectroscopy studies of the oxidation of PdCr indicate that very little PdO forms (ref. 2). A very thin layer of PdO could affect adhesion of an overcoat, for example, but would probably have little effect on the oxidation rate.

Above 870 °C, PdO is thermodynamically unstable and will not form. Weight gains at 900 and 1000 °C must be caused by the oxidation of chromium. Even at lower temperatures,  $\text{Cr}_2\text{O}_3$  has a much higher negative free energy of formation compared to PdO and it is therefore unlikely that PdO plays an important role in the oxidation.

Although palladium can take up an appreciable amount of oxygen into solution without forming a stoichiometric oxide (refs. 12 and 13), such a mechanism is insufficient to account for the weight gains. Therefore, the oxidation of chromium is the only mechanism capable of producing the observed weight gains for any of the TG experiments above 400 °C.

It is difficult to determine the effect of oxygen partial pressure on the oxidation rate. The wire samples were treated in air+argon at an unknown concentration. For the ribbon samples treated at 600 and 800 °C in relatively pure oxygen, the plots cross after approximately 14 hr (fig. 2) whereas for the ribbons treated in air at these temperatures, the curves cross after approximately 2 hr (fig. 3). These data may suggest that oxidation rates were faster in air. However, one must note that these data were collected on different instruments. Also, the ribbons treated in oxygen were corrected to plot specific weight whereas the ribbons treated in air were plotted against weight percent. No conclusive comparisons can be made concerning the effect of oxygen partial pressures.

There is a general trend even though a direct comparison cannot be made between figures 2 and 3 because experimental conditions were not the same. As the temperature increases above 600 °C (up to 900 °C), the oxidation rate decreases. This correlation between the oxidation rate and temperature is observed in all sets of experiments.

It is also difficult to compare ribbons with wires because the purge gasses were different. When weight percent is plotted instead of specific weight, the sample geometry has a surface-to-volume ratio. This effect for the wire samples is approximately twice that for the ribbon samples. Because the exact sample areas were not known, exact comparisons could not be made.

## CONCLUSIONS

The oxidation of PdCr is complex with various kinetics at different temperatures; however, several conclusions can be drawn from the data.

The observed weight gains are related to the formation of  $\text{Cr}_2\text{O}_3$ , which is also the most stable oxide of chromium. The formation of  $\text{Cr}_2\text{O}_3$  is the only oxidation mechanism that can account for the observed weight gains. This result is similar to those from previous studies.

The parabolic weight gain at 600 °C suggests that the rate-limiting step in the oxidation is diffusion through a thickening protective scale. The determined parabolic rate constant,  $1.5 \times 10^{-12} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ , is slightly larger than would be expected for  $\text{Cr}_2\text{O}_3$  growing on pure chromium, but the difference may be a result of the metallic palladium inclusions in the protective oxide scale.

The passivation observed at 700 to 900 °C may be caused by a decrease in the number of short-circuit diffusion paths with time. Metallic palladium, included in the protective  $\text{Cr}_2\text{O}_3$  scale, could provide such short-circuit diffusion paths. At times longer than about 2 hr, the oxidation rate of PdCr decreases with increasing temperature over the temperature range from 600 to about 900 °C.

The increase of oxygen ions causes an increase in oxidation at 1000 °C may be caused by increased diffusion of oxygen ions through the  $\text{Cr}_2\text{O}_3$  layer. Diffusion is expected to increase with increasing temperatures. Since the oxidation above 600 °C is not parabolic, quantitative comparisons cannot be easily made between these temperatures.

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TABLE I.—PARAMETERS USED FOR THERMOGRAVIMETRIC  
ANALYSIS

| Material | Temperature,<br>°C |         | Heating<br>rate,<br>°C/min | Gas<br>composition |
|----------|--------------------|---------|----------------------------|--------------------|
|          | Initial            | Treated |                            |                    |
| Wire     | 40                 | 600     | 10                         | Air+argon          |
| Wire     | 40                 | 800     | 10                         | Air+argon          |
| Wire     | 40                 | 1000    | 10                         | Air+argon          |
| Ribbon   | Room               | 400     | Not determined             | Oxygen             |
|          | Room               | 600     | Not determined             | Oxygen             |
|          | Room               | 800     | Not determined             | Oxygen             |
|          | 40                 | 600     | 5                          | Air                |
|          |                    | 700     | 5                          |                    |
|          |                    | 800     | 10                         |                    |
|          |                    | 900     | 10                         |                    |



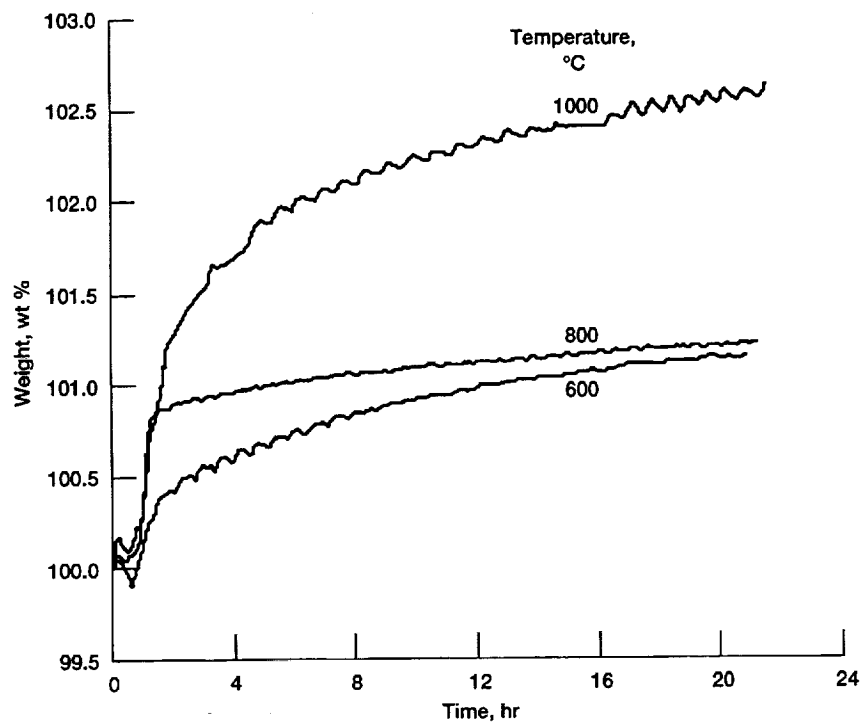


Figure 1.—Thermogravimetric curve of PdCr wires treated in air+argon.

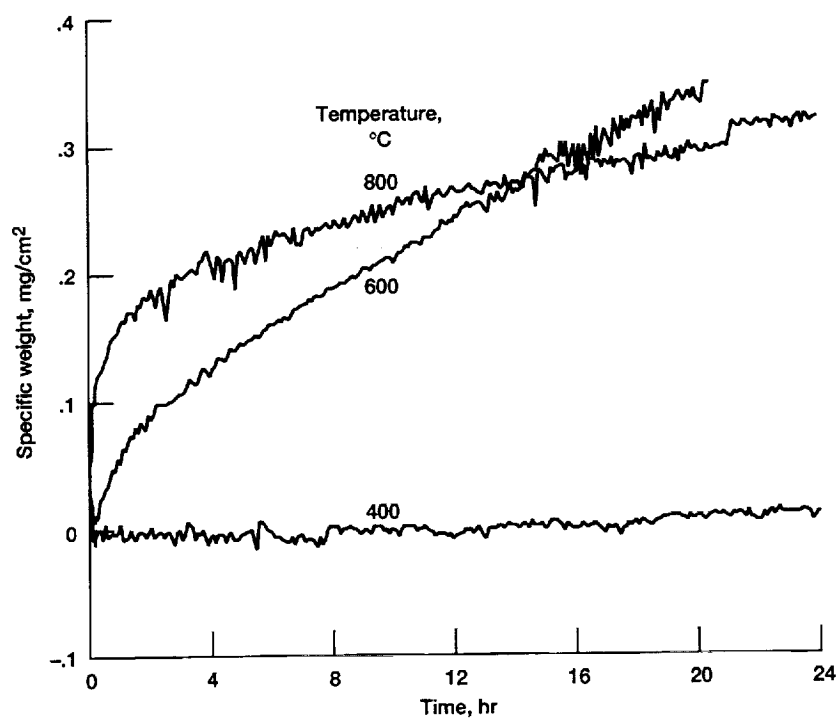


Figure 2.—Thermogravimetric curve of PdCr ribbons treated in oxygen.

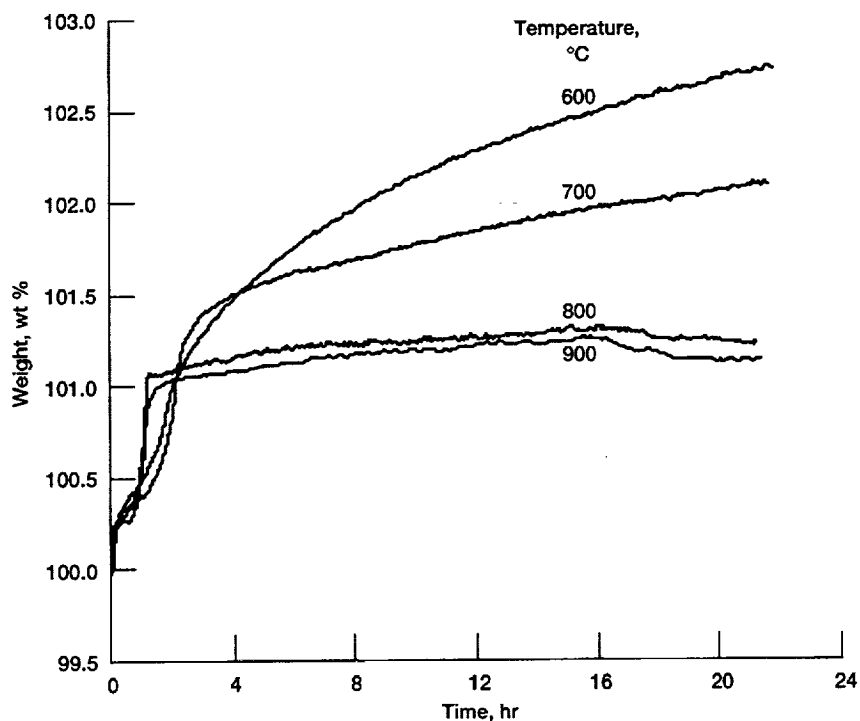


Figure 3.—Thermogravimetric curve of PdCr ribbons treated in air.

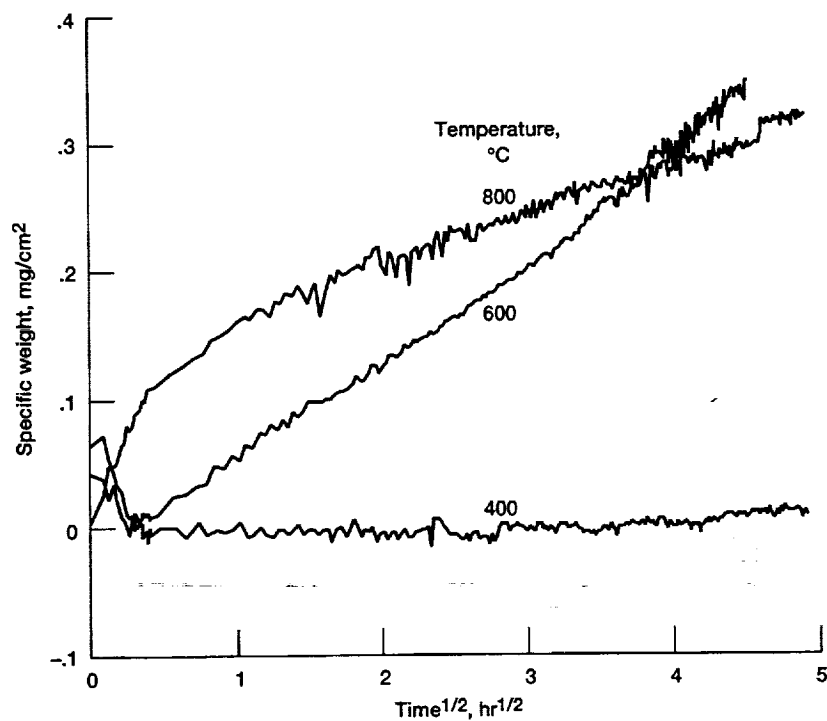


Figure 4.—Thermogravimetric curve of PdCr ribbons treated in oxygen. The straight line portion of the 600 °C run indicates parabolic oxidation.



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